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Inclosed is corrected page 12, which is to be inserted in

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Errata to
AO-20 #1

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In the fabrication of PT 63 X the cesium addition was continued to 2.8 (Cs/O) mole ratio. The photoemission during the cesium addition passed a maximum at 2.0 (Cs/O), the thermionic emission increased to a maximum on cooling the cesium source at 2.4 (Cs/O), but further cesium addition re-sulted in a rapid decrease in the thermionic emission. At 2.8 (Cs/O) the thermionic emission had disappeared and the F_2 response $(\lambda > 775$ m$\mu)$ was negligible. On cooling the tube to room temperature excess cesium was observed condensing on the tube elements which cooled first. After fabri-cation the photoresponse had a maximum at 640 mμ and a long wavelength limit of 800 mμ. The tube was then baked at 150°C for 2 hours and at 130°C for 3.5 hours to distil some of the cesium excess into the cesium source which was maintained at less than 50°C. After sealing the cesium source off, the tube was given a 150°C equilibrating bake. This bake did not re in any significant change in the conduction current or the photoemission as compared to the previous 150°C bake. It is interesting to note that

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Report No. 8

on

Contract DA-44-009eng 405
Project 8-23-02-003

E. N. Lassettre   July 28, 1953

THE OHIO STATE UNIVERSITY
RESEARCH FOUNDATION

REPORT

By

THE OHIO STATE UNIVERSITY
RESEARCH FOUNDATION

COLUMBUS 10, OHIO

Cooperator .... ENGINEER RESEARCH AND DEVELOPMENT
LABORATORIES; Fort Belvoir, Virginia
Contract DA-44-009eng 405
Project 8-23-02-003

Investigation of .... PHOTOEMISSIVE SURFACES

Subject of Report .... Progress Report for Period

.... October 1 to December 31 1952

Submitted by .... E. N. Lassettre

Date July 28, 1953

PHOTOEMISSIVE SURFACES

During this quarterly period the radioactive cesium tracer gross composition and the x-ray diffraction phase identification studies of the photocathode have been completed. The principal results are summarized in the following section and a brief description of the experiments is then presented. Since detailed technical reports on the experimental investigations of the S-1 surface are being prepared, no extensive discussion of the experiments is presented.

1. SUMMARY

The gross composition of S-1 photocathodes prepared at 150° and 190°C has been investigated using radioactive cesium to determine the cesium concentration on the actual photosurface. In this investigation the cathode consisted of a thick evaporated silver film (> 1000 A) on a glass substrate. The investigation has demonstrated that the gross composition of the cathode may vary widely without marked changes in the infrared response characteristics. For good tubes prepared at 190°C the cathode (Cs/O) mole ratio varied from 0.8 to 1.49; whereas for tubes prepared at 150°C the ratio varied from 1.52 to 2.07. It was observed that the silver film thickness and the speed of evaporation affect the characteristics of the oxidation process as well as the characteristics of the final cathode. In addition, it appears that there is a transport of oxygen (as a cesium oxide, probably) if excess cesium is introduced into the tube.

The x-ray diffraction phase identification experiments have demon-
strated that the only cesium oxide detectable in a high sensitivity
good infrared response surface is Cs_2O. Cathodes containing cesium in
excess of Cs_2O (namely Cs_3O) do not exhibit good infrared response
characteristics. It has also been demonstrated that infrared sensitive
surfaces may be prepared at 150°C which contain unreacted silver oxides
and which are stable at room temperature for at least several weeks.

During the preparation of the x-ray sample tubes evidence was ob-
tained which indicates that in the reaction of cesium with the photo-
cathode practically every collision results in chemical reaction.
Consequently the tube geometry may exert a profound influence on the
thermionic and photoelectric characteristics as a function of the time
of cesium addition and the corresponding gross (Cs/O) mole ratio for the
tube.

In the preparation of the massive cathode tube it is frequently
necessary to repeatedly oxidize and heat-treat the cathode to obtain
a surface which oxidizes uniformly during the glow discharge. It has
been observed that massive silver sheet which has been well rinsed
with distilled water just prior to sealing the tube to the vacuum
system consistently oxidizes uniformly during the first glow-discharge
oxidation. It appears that the white deposit frequently formed during
the sealing-off of the end of the pyrex envelope is not completely re-
moved during outgassing and that this substance does interfere with
the oxidation of the silver.

2. GROSS COMPOSITION OF THE PHOTOCATHODE

An investigation has been performed in which the gross Cs/O mole ratio of the photocathodes formed under different experimental conditions was determined. This study was performed by reacting cesium containing a known amount of radioactive Cs^{134} with a known amount of oxygen deposited by a high voltage glow discharge on an evaporated silver film. The actual tube construction and fabrication procedure have been described in previous reports. After phototube processing was completed and the spectral response characteristics determined, the tube envelope was opened, and the cathode removed. The concentration of cesium on the cathode was determined by counting the radioactive cesium with a Geiger counter and comparing this result to that obtained with a set of standard samples containing known amounts of the original tracer cesium mixture. From the total cesium thus determined and the known amount of oxygen deposited, the gross (Cs/O) mole ratio for the cathode was computed. This ratio is referred to as the (Cs/O) count mole ratio. Since the cesium addition to the tube was controlled by a capillary of known dimensions, it was also possible to compute a gross (Cs/O) mole ratio based on the cesium flow rate through the capillary. This ratio differs from the count ratio because of the reaction of cesium with tube elements and the glass envelope, as well as the reaction at the cathode discussed later.

In the tubes prepared earlier at 190°C using an evaporated silver film substrate it was not readily possible to obtain cathodes which were easily oxidized or which developed the desired infrared response during
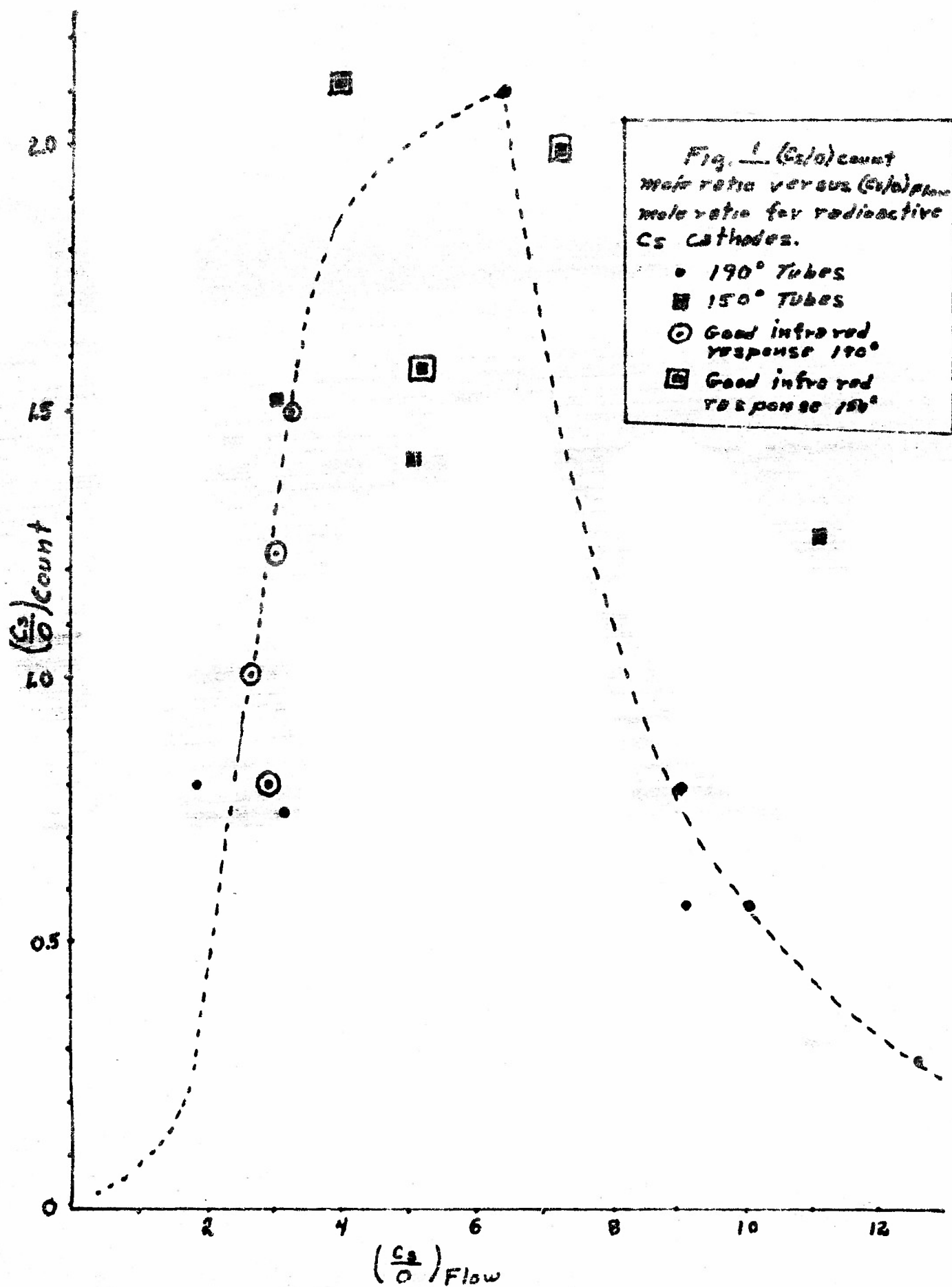
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the reaction with cesium. The cathodes were characterized by the absence of significant thermionic emission during cesium addition and final photoresponses with long wavelength limits of less than 1000 mμ. After considerable experimentation, it was found that good cathodes could be produced consistently by using a thicker evaporated silver film or by using a very slowly evaporated film. These results clearly demonstrated that the thickness and the speed of evaporation of the silver affected the characteristics of both the oxidation process and the photoelectric properties of the final surface.

The composition and photoelectric data for the radioactive cesium tubes which have been prepared at 150° and 190°C are briefly summarized in Table I. It is evident from the data that the gross composition of a good cathode may vary widely (0.8 to 1.49 (Cs/O) count for 190°C tubes) without marked changes in the photoresponse. The infrared sensitive 190°C tubes were prepared by discontinuing the cesium addition shortly beyond the maximum thermionic emission. It was not possible with the limited data to correlate directly the photoelectric characteristics with the gross composition data.

During the preparation of 190°C cathodes the surprising result was obtained that the (Cs/O) count mole ratio decreased when excess cesium was introduced into the tube. (See also Progress Report No. 7) This is illustrated in Fig. 1 where the (Cs/O) count ratio is plotted as a function of the (Cs/O) flow ratio. This result indicates that there is a transport of oxygen from the cathode at 190°C if excess

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TABLE I. RADIOACTIVE Cs TUBES

Tube	Temp.	(Cs/O) Flow	(Cs/O) Count	g. Atom of O x 10^6	Long limit (mμ)	Max. P. E. (mμ)
659-16	190	10.71	0.28	1.27	--	--
659-19	190	2.65	0.74	0.75	860	500
659-28	190	2.23	1.01	3.10	1350	920
659-33	190	5.45	2.10	2.42	--	--
659-42	190	7.80	0.79	1.32	850	615
659-46	190	8.49	0.57	1.26	950	630
1588-111	190	1.57	0.80	1.06	--	370
1588-122	190	2.79	1.49	1.37	1350	950
1588-130	190	2.51	0.80	2.87	1250	920
1588-137	190	2.59	1.23	1.83	1250	935
1588-145	190	7.91	0.57	1.63	--	--
1588-165	150	4.31	2.07	3.82	1250	910
1588-180	150	2.98	1.52	3.27	1300	870
1588-186	150	4.95	1.41	2.08	1150	875
1588-192	150	7.168	1.991	0.88	1300	930
1588-198	150	5.06	1.577	1.73	1350	930
1588-200	150	11.0	1.268	1.198	1200	875

Fig. 1. $(Cs/O)_{count}$ mole ratio versus $(Cs/O)_{Flow}$ mole ratio for radioactive Cs cathodes.

- • 190° Tubes
- ■ 150° Tubes
- ⊙ Good infrared response 190°
- ⊡ Good infrared response 150°

$\left(\dfrac{Cs}{O}\right)_{count}$

$\left(\dfrac{Cs}{O}\right)_{Flow}$

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cesium is introduced. The loss of oxygen could not be related to the total oxygen content of the cathode, the time required for cesium addition, nor the oxidation characteristics of the silver. It appears probable that the loss of oxygen involves the transport of a cesium oxide (possibly Cs_3O) through the gaseous phase.

In the case of tubes fabricated at 150°C there does not appear to be any close correlation between the (Cs/O) count and (Cs/O) flow mole ratios as shown in Fig. 1. The good infrared sensitive 150°C cathodes appear to have a significantly higher (Cs/O) count ratio than the 190°C tubes. At 150°C the cesium oxide, Cs_3O, can be formed as a stable solid phase. Consequently it is surprising that it was not readily possible to prepare cathodes with a (Cs/O) count mole ratio significantly greater than 2.0. It appears that solid Cs_3O must be volatile.

2. PHASE IDENTIFICATION

The identification of the principal components of the photosurface has been accomplished by an x-ray diffraction study of the powder obtained by scraping the photosurface. In this process the massive cathode tube design was modified in that a pyrex x-ray sample capillary tube was sealed to the end of the phototube, and a small razor blade was introduced into the tube. After the tube preparation was completed, the razor blade (manipulated with a permanent magnet) was used to scrape off a sample of the photosurface. The scrapings were shaken into the attached capillary. The phototube was then mounted in a suitable holder and an x-ray photograph of the powder sample was prepared. By this procedure it was possible to minimize the contamination of the sample with foreign materials and

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to use the spectral response as a quality control.

Before describing the results which have been obtained, it is important to note the limitations of the procedure. In the scraping of the powder sample significant quantities of silver are necessarily introduced into the sample. As a result the diffraction patterns of the oxide phases are weak relative to that of the silver and therefore only components at appreciable concentrations ($> \sim 5\%$) are readily detected.

A series of six x-ray sample phototubes have been prepared as shown in Table II. Two tubes PT 42 X and PT 55 X were fabricated at 190°C. In the preparation of PT 42 X the cesium source was cooled at the thermionic emission maximum, and the tube was cooled after the second maximum was passed. In the case of PT 55 X the cesium addition was continued until the stable 190°C thermionic emission surface with cesium source cool was obtained. After fabrication both tubes were given a 130°C bake. The other tubes were fabricated at 150°C in an effort to clarify the reason for the difference in the emission behavior during fabrication at 150 and 190°C. It has been observed that when the cesium source at (Cs/O) mole ratios of 1.0 is cooled, the thermionic emission increases to a stable value for tubes fabricated at 150°C but decreases rapidly to a low value for tubes fabricated at 190°C. In addition several tubes have been prepared at 150°C in which good infrared sensitive surfaces have been obtained at gross tube composition mole ratios between 2.0 and 3.0 (Cs/O). This result suggested that either Cs_3O could contribute to the infrared photoemission or that a cesium sink other than the photosurface existed in the tube.

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TABLE II. X-RAY POWDER SAMPLE PHOTOTUBES

Tube	(Cs/O) Flow	Fab. Temp. °C	Bake Temp. °C	Photo response (mμ)						X-ray result
				Before Bake			After Bake			
				Peak λ	1/2 Height λ	Long λ limit	Peak λ	1/2 height λ	Long λ limit	
PT59X	1.04	150	150	700 and 900	1045	1250	700 and 900	1080	1300	$Ag + Ag_2O \gamma + Cs_2O_3(?)\gamma$
PT65X	1.0	150	150	950	1050	1250	945	1060	1300	Ag
PT42X	Maximum Thermionic Emission	190	126	950	1065	1300	960	1090	1500	$Ag + Cs_2O$
PT55X	1.48	190	130	960	1065	1300	950	1065	1400	$Ag + Cs_2O$
PT58X	2.4	150	150	725	795	920	890	985	1200	$Ag + Cs_2O + Cs_3O(?)$
PT63X	2.8	150	150	640	715	800	650	725	810	$Ag + Cs_2O + Cs_3O$

The x-ray diffraction study of the good infrared cathodes prepared at 190°C demonstrated that the principal cesium oxide present was Cs_2O. Considering the process of the development of photoemission and thermionic emission at 190°C, the results indicate that the infrared photoemitter is crystalline Cs_2O.

In the preparation of PT 59 X and PT 65 X at 150°C, the cesium addition was discontinued at 1.0 (Cs/O). At this stage the top half of the cathode exhibited the color c the original silver oxide, whereas the bottom half appeared to have reacted with cesium to form a dark black to grey surface. The photoresponse of the top half of the cathode was considerably less than the bottom but with only minor differences in the wavelength characteristics of the spectral response curves. Both sections of the tube exhibited infrared sensitiveity. It did not prove feasible to prepare x-ray photographs of samples from the two zones. The x-ray diffraction pattern prepared from the PT 59 X sample exhibited the strong lines characteristic of glow-discharge oxidized silver, and possibly the strongest line of Cs_2O_3. The sample from PT 65 X consisted primarily of silver. The actual oxide concentration in the sample was too low to be detected.

The results on the 1.0 (Cs/O) tubes clearly demonstrate that at 150°C an infrared sensitive surface may be formed with excess silver oxide present. It appears probable that the difference in tube fabrication characteristics for 150° and 190°C at 1.0 Cs/O is related to the rate of decomposition of unreacted silver oxide. It is possible that at 190°C the stable thermionic emitting surface is not formed until the

silver oxides have been reduced and an approximation to phase equilibrium established.

The two-zone appearance of the 1.0 (Cs/O) tubes is undoubtedly related to the molecular beam effect associated with mounting the cesium entrance tube at the base. In the course of the preparation of other x-ray sample tubes, it has been observed that during cesium addition the boundary slowly sweeps the cathode face from bottom to top. In addition, the very rapid decrease in the thermionic emission associated with excess cesium does not occur until the cathode has been covered by the reaction region. This behavior is understandable if it is assumed that practically every cesium collision with the surface results in reaction, and therefore the tube geometry is critically involved in the distribution of cesium on the cathode. It is to be noted that rate of decomposition of the glow discharge silver oxides at 190°C is measureable; however, the rate is sufficiently slow that an appreciable fraction of the oxygen is not lost during the fabricaton of a _massive_ cathode tube at 190°C. It would appear probable that the rate of decomposition at 150°C would be negligible with respect to the processeirg time involved.

Two excess cesium cathodes PT 58 X and PT 63 X were prepared at 150°C. In the case of PT 58 X the cesium addition was discontinued at 2.4 (Cs/O) when the infrared response ($\lambda > 775$ mμ) became negligible compared to the white light response. Cooling the cesium source did not produce a marked change in the thermionic emission. After sealing the cesium source, the tube was baked for two hours at 150°C during which time appreciable thermionic emission was developed. The bake changed

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the spectral response maximum from 752 to 890 mμ, and the long wave-length limit from 800 to 1200 mμ. The x-ray diffraction pattern for this cathode exhibited the powder diffraction lines characteristic of Cs_2O. In the preparation of the photographs unfiltered copper radiation was used to avoid prohibitively long exposures. The diffraction pattern for PT 53 X also contained a series of single crystal spots because of K_α and K_β copper radiation. The majority of the spots could be definitely associated with the presence of some large Cs_2O crystals; however, a pair of spots could possibly be associated with the presence of some Cs_3O crystals.

In the fabrication of PT 63 X the cesium addition was continued to 2.8 (Cs/O) mole ratio. The photoemission during the cesium addition passed a maximum at 2.0 (Cs/O), the thermionic emission increased to a maximum on cooling the cesium source at 2.4 (Cs/O), but further cesium addition resulted in a rapid decrease in the thermionic emission. At 2.8 (Cs/O) the thermionic emission had disappeared and the F_2 response ($\lambda > 775$ mμ) to room temperature excess cesium was observed condensing on the tube elements which cooled first. After fabrication the photoresponse had a maximum at 640 mμ and a long wavelength limit of 800 mμ. The tube was then baked at 150°C for 2 hours and at 130°C for 3.5 hours to distil some of the cesium excess into the cesium source which was maintained at less than 50°C. After sealing the cesium source off, the tube was given a 150°C equilibrating bake. This bake did not result in any significant change in the conduction current or the photoemission as compared to the previous 150°C bake. It is interesting to note that

the conduction current decreased with decreasing temperature and thus the leakage current is not due to metallic conduction. After the bake the spectral response maximum was observed at 650 mμ and the long wave length limit at 810 mμ. The x-ray photograph for this cathode clearly demonstrated the presence of large single crystals of Cs_3O and randomly oriented small crystals of Cs_2O. Thus a cathode definitely containing Cs_3O does not have good infrared response characteristics.

4. GLOW-DISCHARGE OXIDATION

During the early stages in the preparation of the cathodes for x-ray diffraction studies, it was observed that in some tubes it was very difficult to obtain a uniform glow-discharge oxidation of the cathode. It was frequently necessary to oxidize and heat-treat the cathode 3 or 4 times before a uniform oxidation was obtained. In addition it was frequently observed that a very thin hazy white deposit forms in the tube envelope when the end of the pyrex envelope is sealed off. During the initial out-gassing of the tube, the white film was transferred to the cooler portions of the vacuum system. It has been established that the white substance is water soluble and if the interior of the tube is carefully rinsed with distilled water just prior to mounting on the vacuum system the oxidation of the cathode consistently proceeds uniformly over the entire surface. Thus it would appear that the white substance is not completely removed during the out-gassing and can affect the oxidation characteristics of the silver.

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5. CRYSTAL STRUCTURE OF Cs_2O

As mentioned in the last progress report, electron density calculations are being made for the Cs_2O crystal. The first calculations have been completed during the quarter. As the result of these computations an error in a parameter has been found which is of considerable importance. The structure may be roughly visualized as made up of parallel planes of cesium ions which are not quite equally spaced. The distance between one pair of layers is somewhat smaller than between an adjacent pair and these repeat alternately throughout the structure. Oxygen lies between one pair of cesium planes but no oxygen is between the other pair. Because of the low scattering power of oxygen, compared to cesium, it is difficult to decide which of the two alternate positions it occupies. The line sections have shown that the oxygen position is the opposite of that which has previously been assumed. This changed position leads to better agreement between observed and calculated scattering factors. The change does, however, require new electron density calculations which have also been completed. Preparation of a final report on the structure is planned for the near future.

The measurement of magnetic susceptibility and electrical conductivity for Cs_3O is underway. These measurements will be completed before the preparation of the final report on the structure of this crystal. The structure determination on Cs_3O is complete.

Signature Page

to

Report No. 8

on

NP Project 443

NOTE: In submitting this report it is understood that all provisions of the contract between The Foundation and the Cooperator and pertaining to publicity of subject matter will be rigidly observed.

Investigator .... Date ....

Supervisor ....*Edwin N. Lassettre*.......... Date *Aug. 24, 1953*

For The Ohio State University Research Foundation

Executive Director ....*Oran C. Woolpert*.......... Date *8/25/53*